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ENVIRONMENTAL REACTIVITY OF SOLID STATE HYDRIDE MATERIALS

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ABSTRACT

In searching for high gravimetric and volumetric density hydrogen storage systems, it is inevitable that higher energy density materials will be used. In order to make safe and commercially acceptable condensed phase hydrogen storage systems, it is important to understand quantitatively the risks involved in using and handling these materials and to develop appropriate mitigation strategies to handle potential material exposure events. A crucial aspect of the development of risk identification and mitigation strategies is the development of rigorous environmental reactivity testing standards and procedures. This will allow for the identification of potential risks and implementation of risk mitigation strategies. Modified testing procedures for shipping air and/or water sensitive materials, as codified by the United Nations, have been used to evaluate two potential hydrogen storage materials, $2LiBH_4 \cdot MgH_2$ and NH_3BH_3. The modified U.N. procedures include identification of self-reactive substances, pyrophoric substances, and gas-emitting substances with water contact. The results of these tests for air and water contact sensitivity will be compared to the pure material components where appropriate (e.g. $LiBH_4$ and MgH_2). The water contact tests are divided into two scenarios dependent on the hydride to water mole ratio and heat transport characteristics. Air contact tests were run to determine whether a substance will spontaneously react with air in a packed or dispersed form. In the case of the $2LiBH_4 \cdot MgH_2$ material, the results from the hydride mixture compared to the pure materials' results showed the MgH_2 to be the least reactive component and $LiBH_4$ the more reactive. The combined $2LiBH_4 \cdot MgH_2$ resulted in a material having environmental reactivity between these two materials. Relative to $2LiBH_4 \cdot MgH_2$, the chemical hydride NH_3BH_3 was observed to be less environmentally reactive.

1.0 INTRODUCTION

Hydrogen is a viable candidate as an energy storage medium due to its inherent cleanliness upon oxidation and its ready utilization in fuel cell applications. In searching for ever higher gravimetric and volumetric density hydrogen storage materials and systems, it is inevitable that higher energy materials will be studied and used. To make safe and commercially acceptable systems, it is important to understand, quantitatively, the risks involved in using and handling these materials and to develop appropriate safety systems to handle unforeseen accidental events.

The majority of research programs currently underway deal with the development of new solid-state hydrogen storage materials and their reversibility. There have been few programs concentrating on development of systems to utilize these materials and fewer programs still comprehensively dealing with the inherent safety considerations inherent to any system build using these materials. Adherence to international standards for safety will ultimately be required of any energy storage system which commercially exploits these materials. Many of the materials currently being considered as solid state hydrogen storage media are sensitive to air, water and water vapor (insert references). In the spirit of system engineering, it is particularly enlightening to determine the relative environmental reactivity of the various candidate compounds under consideration. By understanding the nature of the environmental reactivity of these materials, amelioration and risk mitigation methods can be devised which will reduce the hazard associated

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with any inadvertent exposure to acceptable levels. Through development of global solid-state hydrogen storage safety programs, it is anticipated that international standards for testing and risk mitigation can be developed and implemented.

The current work is part of the IPHE collaboration (International Partnership for a Hydrogen Economy) that seeks to understand the physical risks involved in synthesis, handling and utilization of these materials as hydrogen storage media as well as development of methods to mitigate these risks which would result in commercially acceptable high density hydrogen storage system designs. A team of laboratories expert in hydrogen storage: Savannah River National Laboratory, Sandia National Laboratory & United Technologies Corp. (USA), Forschungszentrum Karlsruhe (Germany), National Institute for Advanced Industrial Science and Technology (Japan) and Université du Québec à Trois-Rivières (Canada), brings a broad spectrum of expertise in solid sate hydrogen storage and focused to fundamentally understand these phenomenon. This international collaboration will hasten the development and acceptance of these systems.

The objective of the presented study is to fundamentally understand the safety issues associated with solid state hydrogen storage materials through development of standard testing techniques to quantitatively evaluate both materials and systems. The results of these tests will be used to partially understand the fundamental science of environmental reactivity of hydrides and physisorption materials with common environmental compounds and to develop amelioration methods and systems to mitigate the risks to acceptable levels.

2.0 EXPERIMENTAL

2.1 Standardized Materials Testing

A set of materials testing procedures, based on internationally accepted standards drawn from ASTM and United Nations[1] testing procedures, has been defined. These tests will include exposure to air, humidity, water, and proposed heat transfer fluids. The materials of interested are categorized as either reasonably well known (e.g. $NaAlH_4$/2%$TiCl_3$, Mg_2NiH_4, $LaNi_5NH_6$ and $LiH+MgNH_2$), and relatively unknown compounds (e.g. NH_3BH_3, AlH_3, activated carbon and $2LiBH_4+MgH_2$). As part of the collaborative program, these materials will be tested identically to quantitatively determine their reactivity under normally occurring environmental and operating conditions. The materials will be tested in a variety of experimental conditions, including fully charged, partially discharged and fully discharged states in both packed and finely dispersed forms with and without an ignition source.

2.1 Water Reactivity Tests

The purpose of the water reactivity test is to verify if the substance, when in contact with water, burns or emits flammable gases. The experimental details followed UN-RTDG part-3, test-N5 in which three separate tests were conducted. (i) A small quantity (approximately 2 mm diameter) of the test substance was dropped in a trough of distilled water at 20^{o}C. (*Water Immersion Test)* (ii) A small quantity (approximately 2 mm diameter) of the test substance was placed on the center of a filter paper which is floated flat on the surface of distilled water at 20^{o}C in a suitable vessel (i.e. a 250 ml beaker). The filter paper is to keep the substance in one place, under which condition the likelihood of spontaneous ignition of any gas is greatest. (*Surface Contact Test*) (iii) The test substance was formed into a small pile approximately 20 mm high and 30 mm diameter with a hollow in the top. A few drops of water are added to the hollow. If spontaneous ignition occurred

at any stage, the substance is classified as a water reactive substance emitting flammable gases. No further testing is necessary. (*Water Drop Test*)

2.2 Burning Rate Test

The purposes of the burn rate test are the classification of rapidly combustible solids, differentiation of ignitable, rapidly burning and dangerous burning substances and assessment of the relative hazard of rapidly combustible solids. The test procedure details followed UN-RTDG part-3, test-N1 [1]. The powdery hydrogen storage material was deposited as a strip on a platform to measure the burning rate. The powder strip with 250 mm of length and a 100 mm^2 cross-section was ignited from one end and burning propagation time measured for 100 mm after an initial stabilization period. A series of 6 thermocouples was fitted along the axis of burnrate propagation at regular intervals, so that the temperature at a point ~5 mm into the pile could be monitored as a function of time. Additionally, these tests were video recorded to provide qualitative data acquisition, as well as a second manner to reproducibly calculate the burnrate. The substance is classified as Packing Group II if burning time less than 45 seconds.

2.3 Spontaneous Combustion Test

The purpose of the spontaneous combustion test is to classify spontaneously combustible materials into two types: (i) Pyrophoric Substances, solid or liquid mixtures which, even in small quantities, ignite within 5 minutes of coming in contact with air, and (ii) Self-heating substances, substances which, in contact with air and without an energy supply, are liable to self-heating. These substances will ignite only when in large quantities (i.e. kilogram), and after a long period of time (i.e. hours or days).

The details of the test procedure followed UN-RTDG div. 4.2. The powder samples were loaded in 25x25x25 mm cubic baskets made of stainless steel screen with 0.05 mm openings and an uncovered top surface. 3 chromel-alumel thermocouples, with 0.3 mm diameter were inserted into the cubic sample container at positions in the center, face-center, and corner of the powdery sample to monitor temperature. The basket was housed in a cubic container cover made from a stainless steel net with a mesh opening of 0.60 mm, and slightly larger than the sample container. The cube is set in a hot air-circulating oven nominally at 150^{o}C for at least 24 hours or until spontaneous ignition or hazardous self-heating was observed. It was experimental observed that there was a 10^{o}C overshoot of the measured internal oven temperature at setpoint and the nominal setpoint temperature. The changes of the temperature at the chosen locations of the cube were recorded for the duration of the test.

2.4 Pyrophoricity Test

The purpose of the pyrophoricity test is to verify the ability of a solid to ignite on contact with air and determine the time to ignition. The test procedure followed UN-RTDG part-3, test-N2. An aliquot of 1~2 ml of the sample was poured from approximately a one meter height onto a non-combustible surface. Observation was made as to whether the substance ignited during dropping or within 5 minutes of settling. This procedure was performed six times or until a positive result was obtained. The substance was classified as pyrophoric if ignition occurred during one of the free-dropping tests.

2.5 Materials

The raw materials were purchased from commercial vendors and ballmilled to give a uniform starting condition for the tests. Materials were typically SPEX milled in 3g amounts, using 2 xg stainless steel balls and 4 yg stainless steel balls. All materials were handled in an inert atmosphere Ar environment glove box, and exposure to air when in transfer to the testing equipment was minimized as much as possible. In order to discharge the materials, 3-10g

amounts of material were loaded into a pressure manifold and heated to a temperature higher than the literature reported discharge temperature for the material of interest. (REF) The materials were tested according to the U.N. Testing procedures, subject to the modifications described below, for air and water reactivity.

3.0 RESULTS AND DISCUSSION

The results of the air and water reactivity tests are presented below, with the water reactivity tests presented first followed by the results of the air reactivity tests. Test results are provided for the materials $2LiBH_4 \cdot MgH_2$ and NH_3BH_3. The materials that are tested are typically selected in coordination with the Hydrogen Storage Materials Centers of Excellence as being a leading candidate or typical of the majority of materials that are being considered within their center. The materials are also subject to rigorous chemical thermodynamic and kinetic characterizations using sophisticated calorimetric techniques, as reported in companion paper by James *et al*. The results of the the standardized tests and the chemical characterization are being used to support a numerical simulation effort, which is also reported on in the paper by James *et al*. The first material that is discussed is the $2LiBH_4 \cdot MgH_2$ material, which is taken as a representative of complex metal hydride material.

3.1 $2LiBH_4 \cdot MgH_2$

The results of the water reactivity tests for $2LiBH_4 \cdot MgH_2$ in the fully charged state are shown below in Figure 1. Fig1(a) depicts the results from the Water Drop Test, where it can be seen that the material is highly reactive with the addition of a few drops of H_2O to a relatively large amount of the hydride material. In Fig1(b), the results of the Water Immersion Test are shown. The material tends to form a film on the surface of the water, with very small spark-like events noted in some cases. At longer times, it can be seen that gas is evolved from the materials in the film. In Fig1(c), the results of the Surface Contact Test are shown, where it can be seen that the material is immediately reactive with the H_2O soaked filter paper, which is in constant contact with the water bath in the beaker.

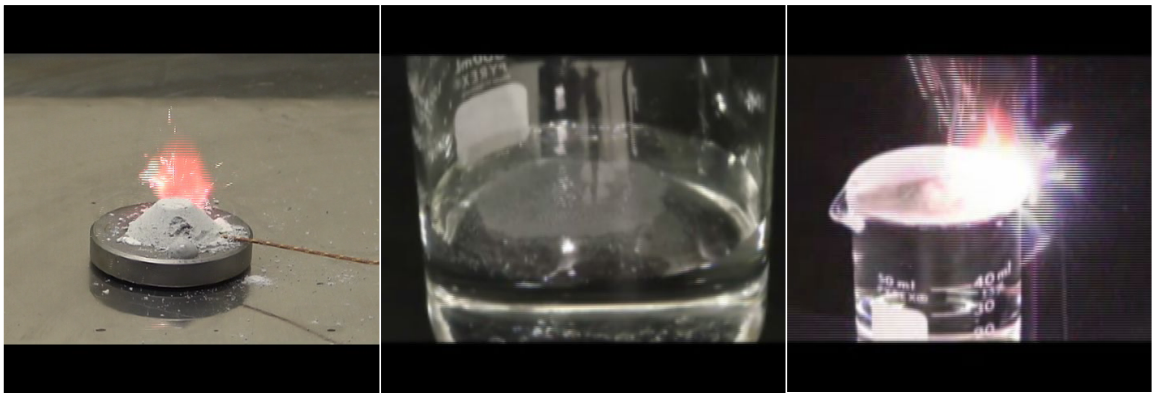

Figure 1. Results from the Water Contact Test for $2LiBH_4 \cdot MgH_2$. a) Reactive event from the water drop test. B) Gas evolution during the water immersion test, and c) Reactive event from the

surface contact test.

The difference in the observed water reactivity of $2LiBH_4 \cdot MgH_2$ in the different scenarios is hypothesized to be the result of the different heat transfer mechanisms in the scenarios and the rate of H_2 and heat generation encountered in the scenario. In the Water Drop Test, H_2 gas is rapidly evolved via the hydrolysis of the constituent $LiBH_4$ and MgH_2 materials; additionally, elemental Mg and Li may also be present in these samples after the ball milling process. These hydrolysis reactions are also well known to be highly exothermic REF, and therefore the possibility of reaching the ignition temperature of the H_2 is possible. In the Water Drop Test, there is no appreciable heat sink to reduce the temperature of the sample and surrounding air. Comparing this to the Water Immersion Test, we can see that H_2 gas is clearly evolved via hydrolysis, as in the Water Drop Test. However, with the presence of the relatively large amount of water in intimate contact with the material, the heat is more quickly wicked away thus preventing a reactive event. The Surface Contact Test is a hybrid between the two scenarios, where the mass transport of the water to the hydride for reaction is impeded by the presence of the filter paper, as is the transfer of the heat to the water which is restricted to only the bottom surface of the pile through the filter. It is obvious that this material is sufficiently reactive to build enough heat energy and H_2 to give rise to a reactive event.

The results of the Self-Heating Test for $2LiBH_4 \cdot MgH_2$ are shown below in Figure 2. Data was collected at 5 minute intervals in this experiment, therefore the number of data points is somewhat sparse over the time interval over which the experiment occurred. On the right of Fig.2 (Fig 2.b), is a background control experiment that was performed on a SiO_2 sample which was loaded into the sample container and placed into the oven. As can be seen, there temperature measured at a point in the interior of the oven, but exterior to the sample, shows the characteristic 10^oC overshoot that is typical of the current setup. The other thermocouples (center, face-center, and corner) all follow the same temperature trajectory. They heat up initially until they reach a steady-state of approximately 150^oC after which the readings remain constant until the heat source from the oven is turned off. The thermocouple reading gradually fall back to room temperature as the oven cools. In contrast, inspection of the Fig 1.a. shows all 4 thermocouples at room temperature at t=0 s. After 5 min, the highest reading is experienced at the face-center location ($T = \sim 400^oC$), with the 2nd highest temperature at the corner ($T = \sim 320^oC$), and the temperature at the center of the sample relatively low at $T = \sim 240^oC$). It should be noted that the criterion for failure of the self-heating test is for the sample to heat above the ambient temperature by 60^oC or more; thus the sample has already experienced dangerous self-heating at this point in the experiment. After the passage of another 5 minutes, the temperature of the center is now the highest measurement ($T = \sim 410^oC$), followed by the temperature of the corner ($T = \sim 340^oC$), followed by the temperature of the face-center ($T = \sim 290^oC$). As time proceeds, the center increases until a maximum reading of $\sim\sim 450^oC$, after which the sample cools until it reaches a steady state of approximately 150^oC, consistent with the background temperature from the SiO_2 sample. These results are interpreted as the procession of a reaction front, which starts at the face-center couple first, then proceeding towards the slightly more interior corner couple, and finally to the central couple. As time proceeds, the relative insulation surrounding the central couple, provided by the reacted material, causes the couple to retain more heat

and reach higher temperatures. These results are consistent with temperature enhanced hydrolysis and oxidation of the hydride materials resulting from the contact with the ambient air in the oven at the elevated temperature of the test.

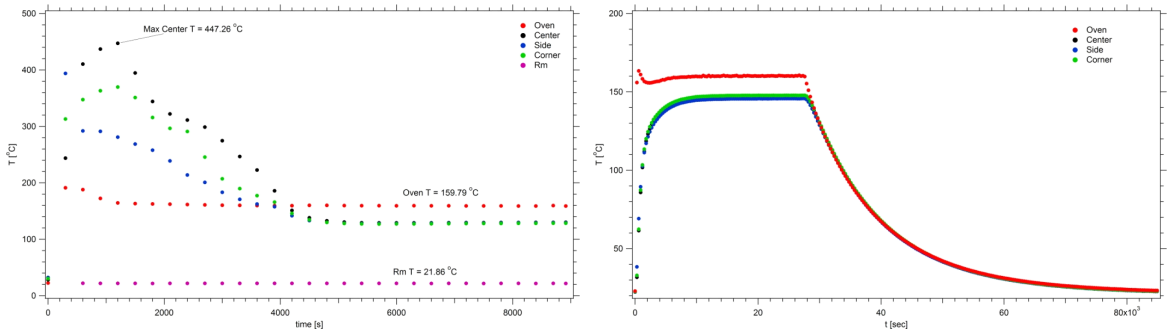

Figure 2. Thermocouple Readings for the Self-Heating Test Performed on $2LiBH_4 \cdot MgH_2$. a) Active $2LiBH_4 \cdot MgH_2$ material. b) SiO_2 material used for background reference.

Shown below in Fig. 3 are the results of the Burn Rate Test for the $2LiBH_4 \cdot MgH_2$ material. In Fig 3.a, a photograph is shown which was taken ~ 5 s into the burn rate test, after which time the flame had propagated the entire length of the sample. It is obvious that the material is combustible by the metrics employed in this test. On the right in Fig 3.b., the results of the thermocouple measurements are shown. In the upper right of the figure is an inset showing a blown-up depiction of the initiation period from 750s – 800s. The burn rate that is reported uses an average of the time optically measured using the video recording data, and the time measured using the thermocouple results. The calculated burn rate for this experiment is 51 mm/s. This value is very similar to the value previously measured for $NaAlH_4$ by Mosher *et al*[2] of 51 mm/s. The lack of symmetry in the thermocouple measurements between the couples which are reflectively displaced from the midpoint of the sample length axis is attributed to non-uniformity of the sample during the test.

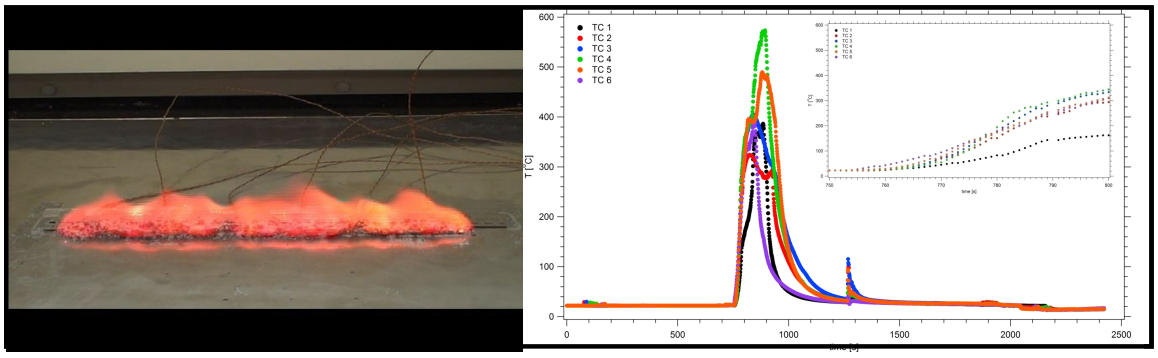

Figure 3. Results of the Burn Rate Test for the $2LiBH_4 \cdot MgH_2$ material. a) Photograph of Burning Material after 5 seconds, b) Thermocouple Readings.

Shown below in Fig. 4 is the result of the U.N. Pyrophoricity test for the $2LiBH_4 \cdot MgH_2$ material after 10 minutes of time. Approximately 1g of the material was dropped into a box with glass sides with the bottom made from industrial grade aluminum sheeting. The test nominally stipulates a 5 min waiting period. It can be seen that there is no reaction of the material in the air

during the material drop, or within the first 10 minutes after the material was allowed to remain on the ground. The test was allowed to continue an additional 5 minutes for a total of 15 minutes, with the same results. Therefore, the material is deemed to non-pyrophoric by the metrics used in this test.

Figure 4. Results of the Pyrophoricity Test of the $2LiBH_4 \cdot MgH_2$ Material 10 Minutes After Air Exposure.

3.2 NH_3BH_3

The results of the Water Reactivity tests for NH_3BH_3 are shown below in Fig. 5. The results are given in the same order as the previous case for $2LiBH_4 \cdot MgH_2$; the Water Drop test is shown in Fig. 5.a, Water Immersion in Fig. 5.b, and the hybrid surface contact is shown in Fig. 5.c. As can be seen from the representative photographs, no discernable reactivity was observed using the metrics associated with the modified U.N. protocols. Whereas the $2LiBH_4 \cdot MgH_2$ material was observed to reactive in all three tests, with significant reactivity observed in the Water Drop and Surface Contact tests, in the case of ammonia borane there is virtually no reactivity. This is consistent with the results of the calorimetric tests reported in the companion paper by James *et al*, as well as other literature on the NH_3BH_3 material. It is significant in light of the high H_2 storage capacity of the NH_3BH_3 material, which is nominally 19.6 wt% (with 12.6 wt% currently achievable under practical reaction conditions). The results would indicate that water contact may not be a significant risk mitigation factor for the NH_3BH_3 materials in the same manner that is might be for a metal hydride based on hydride and borohydride chemical structures.

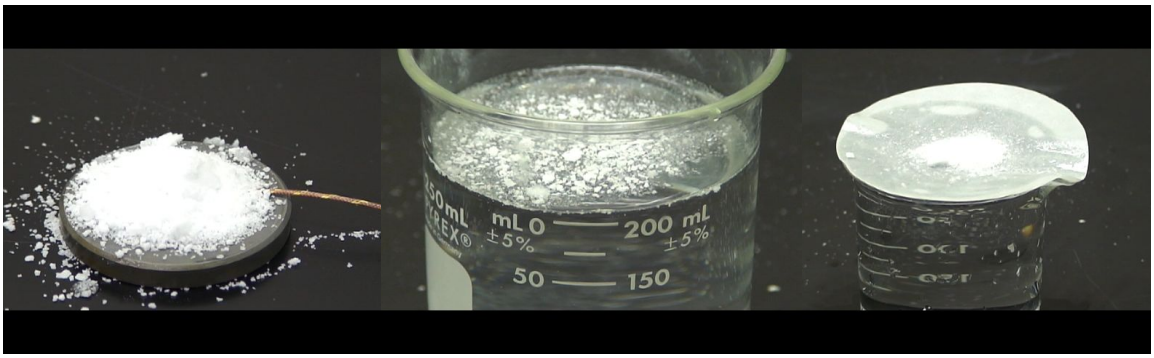

Figure 5. Results from the Water Contact Test for NH_3BH_3. a) water drop test. b) water immersion test, and c) surface contact test.

The results of the Self-Heating Test for the NH_3BH_3 material are shown below in Fig. 6. In this case, data was collected with greater frequency than that for the $2LiBH_4 \cdot MgH_2$ material, so that the temperature ramp of the oven is captured by the ambient thermocouple readings. As can be seen in Fig. 6.a, the set point is hit within about 5 or 6 minutes after the experiment is begun. After sitting at the set point for approximately 5 minutes (for a total of 11 minutes exposure), the NH_3BH_3 undergoes a strong reactivity event inside the oven. At this point in the experiment, some green flame events were observed within the oven (photographic data not available). The ambient thermocouple, which is located just exterior to the sample, rapidly spikes its temperature to ~500°C, after which it falls to around 200°C - 220°C for the remainder of the reactive event. The thermocouples at the face-center and corner locations seem to virtually track one another through the reactive event, reaching a maximum temperature of ~440°C. In Fig. 6.b., a photograph taken after the experiment is shown where it is clear that the NH_3BH_3 material has been extruded through the metal screen of the sample holder. When the material is removed from the exterior of the sample holder, it was found that there was no damage to the sample holder. This is consistent with experimental observations that place the melting point of NH_3BH_3 at 104°C, and the first H_2 desorption temperature at 120°C. It is therefore likely that the NH_3BH_3 material undergoes some degree of melting, followed by H_2 discharge at 120°C. These temperatures are well below the autoignition temperature of H_2 (~571°C); therefore, there must be some degree of temperature-assisted hydrolysis or similar reaction to provide the initial energy for the combustion event.

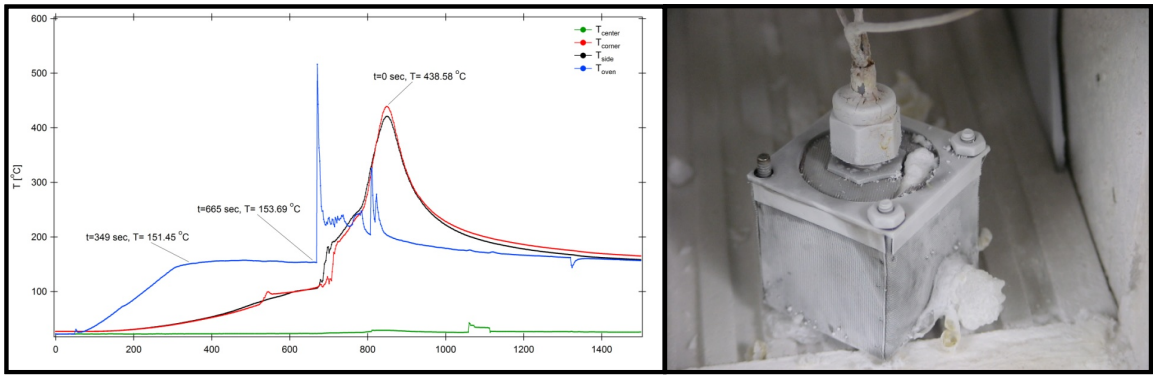

Figure 6. Results of the Self-Heating Test Performed on NH_3BH_3. a) Thermocouple Readings. b) Photograph of Sample Container Showing the Volume Expansion of the NH_3BH_3 Material Upon Heating.

The results of the Burn Rate test for NH_3BH_3 are shown below in Fig. 7. As can be seen, a strong green flame is characteristic of the flame color for boron (B). The collected thermocouple data is shown in Fig 7.b., where it can be seen that the temperature within the burning NH_3BH_3 pile is nearly 500°C, which is approximately the same temperature as the maximum reading of the ambient thermocouple from the Self-Heating test. The calculated burnrate for the NH_3BH_3 material is 33 mm/s, which is 37% slower than the burn rate observed for the $2LiBH_4{\cdot}MgH_2$ and $NaAlH_4$ materials.

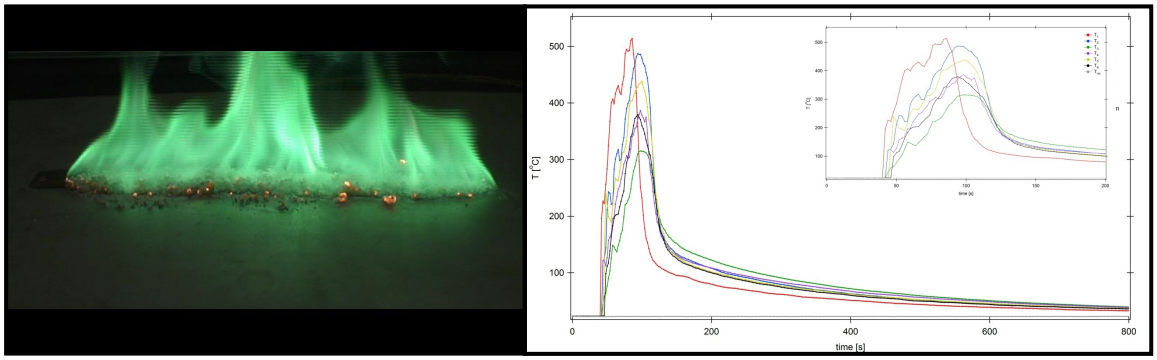

Figure 7. Results of the Burn Rate Test for the NH_3BH_3 material. a) Photograph of Burning Material after 5 seconds, b) Thermocouple Readings.

The findings of the current U.N. testing procedures for $2LiBH_4{\cdot}MgH_2$, along with the findings of colleagues at AIST in Japan for $3Mg(NH_2)_2{\cdot}8LiH$ are shown below in Table 1. It can be easily seen that the most reactive materials are the metal hydrides $2LiBH_4{\cdot}MgH_2$ and $3Mg(NH_2)_2{\cdot}8LiH$, followed by the less environmentally reactive NH_3BH_3. The differences in reactivity may be an important factor in the development of risk mitigation and engineering amelioration strategies developed for systems which employ these types of materials for hydrogen storage applications.

Table 1. Summary of Results of the U.N. Standardized Tests for $2LiBH_4{\cdot}MgH_2$ (SRNL), NH_3BH_3 (SRNL), and $3Mg(NH_2)_2{\cdot}8LiH$ (AIST)

Material / UN Test	State	Pyrophoricity	Self-Heat	Burn Rate	Water Drop	Surface Contact	Water Immersion
$2LiBH_4 \cdot MgH_2$ SRNL	C	No ignition event. Hygroscopic material absorbed H_2O from air.	Self-heated ~300 ºC within 5 min at as T_{oven} = 150 º is approached.	Flame propagated in 5 sec with burn rate of 52 mm/sec.	2 H_2O drops required for near-instant ignition.	Material ignited	No ignition event recorded. Gas evolved at longer times. (5 min)
	D	Not tested	Not tested	Not tested	1 H_2O drop required for near-instant ignition	Reaction observed with no flame	Reaction observed with no flame
NH_3BH_3 SRNL	C	No ignition event. Hygroscopic material absorbed H_2O from air.	Self-heated ~300 ºC within 10 min, 5 min at T_{over}=150 ºC	Flame propagated in 6 sec with burn rate of 33 mm/sec	No reactivity detected	No ignition event recorded. Gas evolved at longer times. (5 min)	No reactivity detected
	D	Not tested	Not tested	Not tested	No reaction	No reaction	No reaction
$3Mg(NH_2)_2 \cdot 8LiH$ AIST	C	Ignition event recorded in room temp experiment	Material failed pyrophoricity test	Flame Propagates at 463 mm/sec	Not tested	Material ignited	Not tested
	D	Ignition event recorded in room temp experiment	Material failed pyrophoricity test	Not tested	Not tested	Not tested	Material ignited

4.0 CONCLUSIONS AND RECOMMENDATIONS

For many years, hydrogen has been discussed as a potential energy storage and carrier medium, in concert with carefully designed production and conversion technologies. The quest to find an appropriate hydrogen storage material is quite challenging on the basis of capacity, thermodynamics and kinetics, and material cost. However, meeting these types of technical targets typical of H_2 storage materials development programs will not be sufficient for practical commercial application of these technologies. The material and the accompanying systems must also be understood and developed with engineering and safety targets in mind as well.

The current work is part of a larger international collaborative partnership geared at gaining this type of basic environmental reactivity characterization data with the intent of not only evaluating candidate materials, but also in developing simple standard methodologies by which future materials may be assessed. The results presented herein are complimented by work conducted within the partnership on basic chemical thermodynamic and kinetic analyses, numerical simulation, and additional materials evaluation techniques.

The materials $2LiBH_4 \cdot MgH_2$ and NH_3BH_3 have been evaluated using modified versions of United Nations test methodologies for shipping and packing identification. In most cases, video recording data is acquired for a given test with a given material; in many cases temperature data is also available to record and monitor the reactive events. It was found that $2LiBH_4 \cdot MgH_2$ is reactive with both air and water under the conditions used in the current tests, with a reactivity that is a mixture of the component $LiBH_4$ and MgH_2 materials. In contrast, it was found that NH_3BH_3 is relatively inert to water reactivity, but is reactive with air under the test conditions. Both of these materials are less reactive than the $3Mg(NH_2)_2 \cdot 8LiH$ material that was tested by colleagues at AIST.

With the risks thus identified, users of these materials, either in the laboratory or in prototype development, must take the proper safeguards to minimize the probability of the loss of property or personal injury. These results, in combination with the thermodynamic and kinetic analysis,

are being used to develop risk mitigation strategies for the hydride materials that have been considered within the program thus far. Future work will consider additional materials such as AlH_3 and the use of numerical simulations to evaluate critical environmental exposure scenarios, with a strong focus on the implementation of the results from these standardized tests for system optimization.

5.0 ACKNOWLEDGEMENTS

[1] DOT/UN Doc., *Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*, 3rd Revised Ed., ISBN 92-1-139068-0, (1999).

[2] Mosher *et al*, **446**, *J. Alloys and Compounds*, pp. 707 (2007)